Orbital measures in non-equilibrium statistical mechanics: the Onsager relations

Short title: Orbital Measures in Statistical Mechanics

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Physics abstracts numbers: 05.45.+b, 05.60.+w, 05.70.Ln
AMS classification unmbers: 82C05, 70F25, 82C70

February 5, 2008

Abstract

We assume that the properties of nonequilibrium stationary states of systems of particles can be expressed in terms of weighted orbital measures, i.e. through periodic orbit expansions. This allows us to derive the Onsager relations for systems of N particles subject to a Gaussian thermostat, under the assumption that the entropy production rate is equal to the phase space contraction rate. Moreover, this also allows us to prove that the relevant transport coefficients are not negative. In the appendix we give an argument for the proper way of treating grazing collisions, a source of possible singularities in the dynamics.

1 Introduction

Very recently a number of proofs have been presented of the Onsager reciprocal relations (OR) in non-equilibrium stationary states based on dynamical systems theory [1, 2, 3]. There, the earlier assumption of Refs.[4, 5], i.e. that the dynamics of systems of particles could be regarded as "Anosov" for practical purposes,[1] was used to characterize the relevant stationary distributions. Consequently, such distributions were conjectured to be of the kind first investigated by Ya. Sinai, D. Ruelle and R. Bowen (SRB distributions) [6]. This assumption makes

[1]For completeness, the main assumption of Ref.[5], p.935 states that:
A reversible, many particle system in a stationary state, can be regarded as a transitive Anosov system, for the purpose of computing its macroscopic properties.

possible a generalization to nonequilibrium stationary states of the classical equilibrium ensembles for the probability to find a system in a certain phase in phase space. In particular, this can be done by attributing to the absolute values of the Jacobian of the dynamics restricted to the unstable manifolds, a meaning connected to that of the Boltzmann factor of the canonical ensemble (see subsection 2.2 below, and see Ref.[7] for numerical experiments meant to justify the connection). Use of such techniques lead to a fluctuation theorem −first investigated in Ref.[8, 4, 5] and further confirmed by a variety of computer experiments [9, 10]− and to the above mentioned proofs of the OR.

There are two representations of the SRB distribution which have been used in practice so far: the Markov partition method of Ref.[5], and the periodic orbit (or cycle) expansions (POE) (see, e.g. Refs.[11, 12, 13, 14]) used, for instance, in Refs.[15, 16, 17, 18]. Here, we present an approach to the proof of the OR based on the assumption that the stationary distribution can be expressed in terms of POE, and on analyticity conditions on the properties of the relevant orbits. The point is not to improve on the quite general proof of Ref.[3], but to show that a different approach with different assumptions can lead to similar results, thus shedding new light on the precise connection between the OR in statistical mechanics and the dynamics of mechanical systems. Periodic orbit expansions are also used, here, for a proof that the transport coefficients of our systems are nonnegative, following in part ideas developed previously in Ref.[19] (see also the paper by D. Ruelle, Ref.[20]) based on the equality of phase space contraction rate and entropy production rate.

The possibility of describing the stationary states of systems of particles in terms of POE is implied by the assumptions of Refs.[4, 5],[2] but the actual range of applicability could be different (see next section). The importance of this approach lies in the fact that, although the practical implementation of the POE for a system of many particles is exceedingly difficult (practically impossible with present day technology), its mathematical expression can be used for formal proofs of properties of real systems. Moreover, the validity of given results obtained in terms of POE can be tested directly on simple models of statistical mechanical interest, by means of modern computers. In fact, POE have been succesfully applied in numerical simulations of one particle systems, such as various (periodic) Lorentz gas models, see e.g. Refs.[7, 15, 16, 17, 18]. In this respect, it is also important to note that the efficiency of this kind of numerical studies can be greatly enhanced, as recently shown in Ref.[21], thus making the numerical implemetation of POE conceivable for more complex systems.

2 Properties of transport coefficients from POE

2.1 Preliminaries

In this paper, we concentrate on a d-dimensional system of N interacting particles, subject to external fields of force (whose strength is gauged by ν parameters), and subject to a Gaussian thermostat [22]. Moreover, in order to make use of the techniques of dynamical system theory,

In other words, if the (possible) deviations of the dynamics from the Anosov conditions bear no consequence for the calculations of the quantities of physical interest, they can be considered as irrelevant. In that case, the system will be called "Anosov-like".

[2] If the system under study is really Anosov, weighted averages of smooth functions evaluated over periodic orbits do converge to the averages computed with the SRB distribution (see e.g. Refs.[11, 12, 13, 14]), despite the fact that periodic orbits cover but a set of zero (Lebesgue and natural) measure. If the system is only "Anosov-like", POE should work as well, at least for the calculations of the physically interesting quantites. However, in this paper we will assume the validity of POE only for the calculation of the average currents, in order to limit the assumptions as much as possible.

we impose periodic boundary conditions on our models. In particular, the equations of motion we consider take the form

$$\dot{\mathbf{q}}_i = \frac{\mathbf{p}_i}{m_i} \ , \quad \dot{\mathbf{p}}_i = \mathbf{\Phi}_i(\mathbf{q}) + \mathbf{F}_i(\mathbf{G}) - \alpha(\mathbf{p},\mathbf{q})\mathbf{p}_i \ , \quad i = 1, ..., N \ , \tag{1}$$

where $\alpha(\mathbf{p},\mathbf{q})$ characterizes the Gaussian thermostat and is determined by the constraint one wants to implement (e.g. fixing the value of a special dynamical quantity). Also, $\mathbf{q}_i$, $\mathbf{p}_i$ and m_i are respectively the coordinates, the momentum and the mass of the ith particle, with $(\mathbf{p},\mathbf{q}) = ((\mathbf{p}_i)_{i=1}^N, (\mathbf{q}_i)_{i=1}^N)$; $\mathbf{\Phi}_i$ is the force on particle i due to the interactions with the other particles; and $\mathbf{F}_i$ is the action of the external fields on the ith particle, which depends on the values of the parameters $\mathbf{G} = (G_1, ..., G_\nu)$. The purpose of the Gaussian thermostat is to make such an N-particle system reach a stationary state when the fields are "switched on", starting from a given initial distribution in phase space. We assume that when $\mathbf{G}$ vanishes, the external forces $\mathbf{F}_i$ and the thermostat coupling α also vanish, making the stationary state an equilibrium state.

The particular constraint we impose on our models is that the total energy remains fixed in time (i.e. we use an iso-energetic thermostat). This yields

$$\alpha(\Gamma;\mathbf{G}) = \frac{1}{2K}\sum_{i=1}^N \frac{\mathbf{p}_i \cdot \mathbf{F}_i(\mathbf{G})}{m_i} \ ; \qquad K = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m_i} \tag{2}$$

where $\Gamma = (\mathbf{p},\mathbf{q})$ stands for a generic point in the phase space, and K is the total kinetic energy of the system.[3] Once the stationary state has been achieved, the periodic boundary conditions[4] imply that there is an elementary cell (EC), Ω say, whose replicas cover the whole $(2dN)$-dimensional phase space, and there is a time evolution on Ω, denoted by S_t, which represents the dynamics of the N particles in Ω. One may also consider the dynamics with respect to a given Poincaré section, $\mathcal{P}$ say, and the timing events for the definition of $\mathcal{P}$ may be chosen to be the collisions between particles. When the interacting potentials are soft, this can be done by calling a collision the event in which two or more particles come within a certain distance of each other [5].

By identifying the phase space contraction rate for the dynamics $-$the divergence of the right hand side of Eqs.(1)$-$ with the (microscopic) entropy production rate, we define the ν (microscopic) **currents** as

$$\mathbf{J}(\Gamma;\mathbf{G}) = \nabla_{\mathbf{G}}\alpha(\Gamma;\mathbf{G}) \equiv (J_1, ..., J_\nu)(\Gamma;\mathbf{G}) \ . \tag{3}$$

This definition of current was first adopted in Ref.[2], and also used in Refs.[3, 19].

In order to develop our analysis in terms of POE, we need that Unstable Periodic Orbits (UPOs) be densely embedded in the support of the natural measure of the system and, if they are,[5] we must characterize their properties. In the first place, UPOs are orbits with at least one positive Lyapunov exponent, and it is convenient to collect them in sets of orbits with a fixed number of collisions. For instance, denote by $P_n(G)$ the set of orbits within which n collisions occur. Then, we let $\omega(G)$ indicate a generic element of $P_n(G)$, and $\tau_{\omega(G)}$ its period. Given

[3] In case of hard core particles, the iso-energetic constraint coincides with the iso-kinetic one, i.e. with the constraint of constant kinetic energy.

[4] Periodic boundaries may look as a rather restricitve condition. However, one should keep in mind that Ω can be arbitrarily large and complex, as long as it may be used to periodically tile the infinite phase space.

[5] Typical dynamical systems whose UPOs are dense in the support of the natural measure are those verifying the axiom-A conditions. Indeed, for such systems the density condition is part of their very definition.

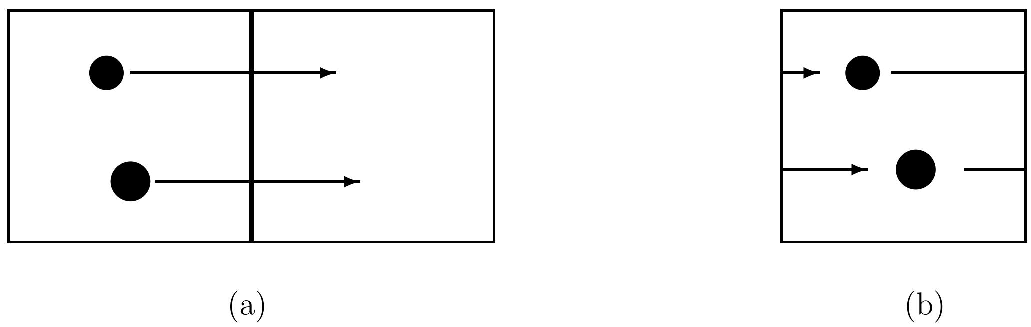

Figure 1: The equivalence between the dynamics in the EC and those in the full phase space. a) Trajectories of two black round particles in the infinite phase space where they move never returning to the same point. Only two adjacent cells, out of the infinitely many which tile the phase space, are drawn. b) Representation of the situation (a) in the EC, where the orbits appear to be periodic. To average any quantity over the trajectories in (a) is the same as to average that quantity over the trajectories in (b), as long as the actual diplacements are accounted for.

any orbit $\omega(G)$, with Lyapunov exponents $\lambda_{\omega(G),1} \geq \lambda_{\omega(G),2} \geq ... \geq \lambda_{\omega(G),2dN}$, we consider the following quantity:

$$\Lambda^{-1}_{\omega(G),u} = \exp\left(-\tau_{\omega(G)} \sum{}' \lambda_{\omega(G),j}\right) , \tag{4}$$

where $\lambda_{\omega(G),j}$ is the j-th Lyapunov exponent of orbit $\omega(G)$, and the prime on the symbol $\sum$ indicates that the sum runs over the *positive* exponents only. The subscript u on the left hand side of Eq.(4) says that $\Lambda_{\omega(G),u}$ is computed restricting the dynamics to the unstable manifold. Notice that $\Lambda_{\omega(G),u}$ is a measure of the instability in the phase space of $\omega(G)$, and it constitutes the basic ingredient in any POE, i.e. it is part of the (unnormalized) weight attributed to $\omega(G)$. In particular, the less unstable the UPO, the larger its weight, as explained in Section 2.2.

For the study of transport in our particle systems, it is interesting to consider the total displacement of the single particles during a whole period of a UPO. In this respect, given $\omega(G)$, it is important to recall that the displacement of the jth particle at the end of one period of $\omega(G)$, $\triangle\mathbf{q}_{j,\omega(G)}$, does not necessarily vanish. When it does not, also the average current associated with $\omega(G)$ may not vanish. Here the average current is the integral of $\nabla_{\mathbf{G}}\alpha$ over the UPO (that is, the cumulative current $\mathbf{I}_\omega$ defined below in Eq.(5)), divided by the period $\tau_{\omega(G)}$. For this reason, it makes sense to talk of currents associated with a UPO although, at first sight, it may look strange. Indeed, the periodic boundary conditions impose translation invariance symmetry along the directions of the lattice vectors in the stationary state. Hence, to follow a trajectory which never returns to the cell where it started from, is equivalent to following its translated image in the EC. See, e.g., Fig.1: the trajectories of the round black particles in the full phase space do not close. However, they can be followed in the EC, where they appear to close producing a periodic orbit. Clearly, to average quantities over the open paths −the real paths in phase space− is the same as averaging them over the images of such paths in the EC, as long as one keeps track of the actual distance covered during the motion. In this sense, when we speak of periodic orbits, we mean all those that are such in the EC. In particular, if the particles in Fig.1 carry the same charge c, the side of the EC is ℓ, and the

period of the orbit is τ, the relevant current is $2c\ell/\tau$. We remark again that it is the presence of the periodic boundary conditions which, *in the stationary state*, allows us to map the infinite system into a finite one: the EC. Away from the stationary state, or in the case that we do not have periodic boundary conditions (like in the random Lorentz gas), the techniques of dynamical system theory fail to apply in this simple manner.

2.2 Conditions

The present paper rests on Assumptions 1. and 2. below which, similarly to those of Refs.[4, 5], are empirically motivated. In particular, our assumptions were inspired by the numerical results presented in Refs.[7, 15, 16, 17, 18] and, in a broader sense, by those of Ref.[8].

Let us introduce the quantity $\mathbf{I}_{\omega(G)}$, the **cumulative current** associated with $\omega(G) \in P_n(G)$:

$$\mathbf{I}_{\omega(G)} = \int_{\omega(G)} \mathbf{J}(S_t \Gamma_{\omega(G)}) \; dt \; , \tag{5}$$

where the integral is carried over one period of $\omega(G)$, and $S_t\Gamma_{\omega(G)}$ is the point representing the state of the system at time t, if it was $\Gamma_{\omega(G)} \in \omega(G)$ at $t = 0$. Then, our first assumption can be formulated as follows.

Assumption 1 (Existence and representation of stationary states). *The dynamical system (Ω, S_t) describing a reversible many-particle system obeys the "Extended zero-th law" of Refs.[4, 5], at least for what concerns the currents. Then, letting μ_G be the corresponding (SRB) stationary distribution, we can write*

$$\langle \mathbf{J} \rangle_\Omega (\mathbf{G}) \equiv \lim_{T\to\infty} \frac{1}{T} \int_0^T \mathbf{J}(S_t\Gamma) \; dt = \int_\Omega \mathbf{J}(\Gamma) \; d\mu_G(\Gamma) \; , \tag{6}$$

for (Lebesgue) almost all $\Gamma \in \Omega$. Also, the phase space average of $\mathbf{J}$ with distribution μ_G can be given in terms of the following POE:

$$\langle \mathbf{J} \rangle_\Omega (\mathbf{G}) = \lim_{n\to\infty} \frac{\sum_{\omega\in P_n(G)} \tau_\omega \Lambda_{\omega,u}^{-1} \mathbf{I}_\omega / \tau_\omega}{\sum_{\omega\in P_n(G)} \tau_\omega \Lambda_{\omega,u}^{-1}} = \lim_{n\to\infty} \frac{\sum_{\omega\in P_n(G)} \Lambda_{\omega,u}^{-1} \mathbf{I}_\omega}{\sum_{\omega\in P_n(G)} \tau_\omega \Lambda_{\omega,u}^{-1}} \; . \tag{7}$$

Equation (7) expresses the current as a limit of weighted averages of orbital average currents, where the weights have the suggestive form

$$\tau_\omega \Lambda_{\omega,u}^{-1} = (\text{time spent in } \omega) \times (\text{inverse of instability of } \omega) \; , \tag{8}$$

apart from a normalization factor. This weight associates the points of a given region of phase space with a probability and is larger for longer UPOs, while it is smaller for more unstable UPOs. It is in this sense that $\tau_\omega \Lambda_{\omega,u}^{-1}$ plays a role similar to that of the Boltzmann factor in the canonical ensemble.

Let us denote by $\langle \mathbf{J} \rangle^{(n)}$ the "n-th order UPO approximation" of the current, i.e.:

$$\langle \mathbf{J} \rangle^{(n)} (\mathbf{G}) = \frac{\sum_{\omega\in P_n(G)} \Lambda_{\omega,u}^{-1} \mathbf{I}_\omega}{\sum_{\omega\in P_n(G)} \tau_\omega \Lambda_{\omega,u}^{-1}} \; , \tag{9}$$

where all properties of a given UPO, ω say, depend on $\mathbf{G}$, because ω is taken from the set $P_n(G)$.

Assumption 2 (Properties near equilibrium). *There is a positive constant ρ such that for $|\mathbf{G}|$ (the modulus of $\mathbf{G}$) smaller than ρ we have:*

- **a.** *the period $\tau_{\omega(G)}$, the stability weight $\Lambda^{-1}_{\omega(G),u}$, and the thermostat coupling $\alpha(S_t\Gamma_\omega;\mathbf{G})$, are "left" and "right" analytic*[6] *with respect to all the components of $\mathbf{G}$, for all $\omega(G) \in P_n(G)$, all $n \in I\!N$, and all $t \geq 0$.*
- **b.** $\{\partial_{G_i}\langle\mathbf{J}\rangle^{(n)}(\mathbf{G})\}$, *converges uniformly to a limit as $n \to \infty$, for $i = 1, ..., \nu$.*
- **c.** *The support of μ_G is dense in Ω.*

In particular, this assumption implies the existence of constants $\mathbf{a}^+_\omega, \mathbf{a}^-_\omega, \mathbf{b}^+_\omega, \mathbf{b}^-_\omega, \mathbf{c}^+_\omega$ and $\mathbf{c}^-_\omega$ in $I\!R^\nu$ such that

$$\tau_{\omega(G)} = \tau_{\omega(0)} + \mathbf{a}_\omega \cdot \mathbf{G} + o(G^2) \; , \tag{10}$$

$$\Lambda^{-1}_{\omega(G),u} = \Lambda^{-1}_{\omega(0),u} + \mathbf{b}_\omega \cdot \mathbf{G} + o(G^2) \; , \tag{11}$$

$$\alpha(S_t\Gamma_{\omega(G)}) = \mathbf{c}_{\omega(0)}(S_t\Gamma_{\omega(0)}) \cdot \mathbf{G} + o(G^2) \; , \tag{12}$$

where the i-th component of $\mathbf{r}_\omega$, $r_{\omega,i}$ say, for $\mathbf{r} = \mathbf{a}, \mathbf{b}, \mathbf{c}$, equals $r^+_{\omega,i}$ when $G_i > 0$, and $r_{\omega,i} = r^-_{\omega,i}$ for $G_i < 0$. The necessity for left and right analyticity emerges in the case of special geometries, i.e. as a consequence of the actual shape of the particles and of the medium where they move. There are cases, indeed, such that reversing the sign of the components of $\mathbf{G}$ may require a change in the values of the constants $\mathbf{a}$, $\mathbf{b}$ and $\mathbf{c}$ above, so that only the left and the right analyticity around $G_i = 0$, for all i, hold. For our purpose, this is sufficient, but in the case we have full analyticity at $\mathbf{G} = 0$, some approximations can be improved, as explained below, after Theorem 1.

Assumptions 1. and 2. are needed here to justify the calculations of subsections 2.3 and 2.4 but, similarly to the assumptions of Refs.[4, 5], they cannot be validated at present on the sole grounds of the given dynamics. Only *a posteriori* we can check whether using them we are led into some kind of inconsistency or not. However, to accept them as possibly valid (*a priori*) we may rely on the evidence accumulated so far in the literature, e.g. on several studies of the nonequilibrium Lorentz gas like Refs.[16, 18, 23] and others. In particular, Assumption 2.a is also in agreement with the discussion of pp.949-950 of Ref.[5], where it is argued that the transition from equilibrium to nonequilibrium stationary states, with small forcing, should be seen as producing "... an insignificant deformation of the unstable manifold W^u_O ...", i.e. of the unstable manifold of a given periodic point. Similarly, one may argue that the properties of periodic orbits will only change little for small changes in the fields. As a matter of fact, the periodic (trianglar lattice) Lorentz gas has been used to test many orbits to high numerical precision in order to see whether their contributions to numerator and denominator of Eq.(7) are smooth in the field. The result is that they appear to be smooth [18], with the only exceptions of orbits with grazing collisions, i.e. orbits which suddenly appear or disappear from the phase space, when the field is varied ever so slightly. However, it does not seem that such orbits should concern us. In the first place, they do not exist if the interactions are

[6]Given a function $f : I\!R \to I\!R$, and a constant $\rho > 0$, we say that f is *left analytic* in $(-\rho, 0]$ if there are constants f_0 and r^- in $I\!R$ such that $f(x) = f_0 + r^-x + o(x^2)$, for all $x \in (-\rho, 0]$. Similarly, we say that f is *right analytic* in $[0, \rho)$ if there are constants f_0 and r^+ in $I\!R$ such that $f(x) = f_0 + r^+x + o(x^2)$, for all $x \in [0, \rho)$. Thus, a function which is analytic in a neighborhood of zero is left and right analytic, and has $r^- = r^+$. However, f could be left and right analytic without its derivatives being defined at $x = 0$. Here $o(x^2)$ is to be understood as a term of second order in x, negligible with respect to the other terms for all x in the relevant intervals.

soft, and hard core interactions could be seen as a limiting case of soft core ones, Ref.[24]. Also, the numerical tests of Refs.[7, 17, 18] have not evidenced any difficulty linked to this problem, because the orbits with grazing collisions were a very small fraction of the whole, with negligible weight each. In the Appendix, we give an argument to justify why these orbits should always be assigned a vanishing weight in the expansion Eq.(7).
A few further remarks are in order.

Assumption 2. plays for us the role of the differentiability of SRB measures in Ref.[3], but it may appear as rather strong. On the other hand, this assumption may be relaxed in various ways, and it is supported to a good extent both by numerical studies of simple systems, and by intuition, as noted above. In practice, we observed that for small changes in the field the orbits change very little in shape which, in turn, determines their properties such as their period, stability, α etc. Furthermore, it is important to note that we do not require that our conditions hold for very general functions of phase. On the contrary, we restrict the validity of our conditions to very special quantities −the phase space contraction rate and its derivatives− which are easily seen to have particularly good properties in the dynamics of many interesting maps.

A comparison between Assumption 1. and the assumptions of Ref.[5] shows that the latter directly refer to the dynamics of the system, i.e. to the properties of the equations of motion and of the space in which the motion takes place. Our assumption, instead, refers to the stationary measure, which is not the dynamics but only a result of the dynamics. Therefore, Assumption 1. is valid if the system is Anosov or axiom-A (hence, also if the assumptions of Ref.[5] hold) but it could still remain valid even for dynamics of a different kind. On the other hand, our assumption is not as fundamental because, for instance, it does not provide us with a direct way of estimating the errors connected with the n-th order UPO approximations of the POE.

2.3 Derivation of the Onsager reciprocity relations

We can now prove the validity of Onsager's relations for the systems verifying our assumptions (which we take to be general N-particle systems subject to an iso-energetic Gaussian thermostat). The proof proceeds as follows. First, we consider the n-th order UPO approximation of Eq.(7), and we expand to first order in $\mathbf{G}$ the resulting expressions. Then, we group together the contributions of periodic orbits with opposite currents, in order to use the relation called *Lyapunov sum rule* in Ref.[19]. This is a relation between the parameter α and the Lyapunov exponents associated with a given periodic orbit (see Eq.(17) below). This allows us to find a symmetry between different derivatives of the n-th order UPO approximate current. Finally, exploiting Assumption 2. we interchange the derivative with taking the infinite period limit operation, to obtain the desired result. The major ingredient in these calculations is the time reversal symmetry of the equations of motion, together with the density of the attractor in the phase space. Indeed, it is because of these two features that we can write Eqs.(14,15,16) below.

Using the assumed analyticity in the fields of the period and of the stability weight (Eqs.(10,11)), we can expand the denominator of Eq.(9) to first order in $\mathbf{G}$ and obtain

$$\langle \mathbf{J} \rangle^{(n)}(\mathbf{G}) = \frac{\sum_{\omega\in P_n(G)} \Lambda_{\omega,u}^{-1} \mathbf{I}_\omega}{\sum_{\omega\in P_n(G)} \tau_{\omega(0)} \Lambda_{\omega(0),u}^{-1}} \left[1 - \frac{\sum_{\omega\in P_n(G)} \tau_{\omega(0)} \mathbf{b}_\omega + \Lambda_{\omega(0),u}^{-1} \mathbf{a}_\omega}{\sum_{\omega\in P_n(G)} \tau_{\omega(0)} \Lambda_{\omega(0),u}^{-1}} \cdot \mathbf{G} + o(G^2) \right] . \tag{13}$$

Then, the time reversibility of Eqs.(1), combined with the density of the relevant attractor in phase space, guarantee that for every orbit $\omega \in P_n(G)$ there is another orbit $-\omega \in P_n(G)$ with equal period and opposite cumulative current $\mathbf{I}$,[7] i.e.:

$$\tau_{-\omega(G)} = \tau_{\omega(G)} \ , \quad \mathbf{I}_{-\omega(G)} = -\mathbf{I}_{\omega(G)} \ . \tag{14}$$

Hence, by grouping together such pairs of orbits, we get:

$$\sum_{\omega\in P_n(G)} \Lambda_{\omega,u}^{-1} \mathbf{I}_\omega = \sum_{\omega\in P_n^+(G)} \left(\Lambda_{\omega,u}^{-1} - \Lambda_{-\omega,u}^{-1} \right) \mathbf{I}_\omega = \sum_{\omega\in P_n^+(G)} \mathbf{I}_\omega \Lambda_{\omega,u}^{-1} \left(1 - \Lambda_\omega\right) \ , \tag{15}$$

where $\omega \in P_n^+(G)$ if it has n collisions and $\int_\omega \alpha(S_t\Gamma_\omega) dt > 0$,[8] and

$$\Lambda_\omega \equiv \exp\left(\tau_\omega \sum_{j=1}^{2dN} \lambda_{\omega,j} \right) \ , \tag{16}$$

where the sum this time involves *all* the Lyapunov exponents of ω. The Lyapunov sum rule for a periodic orbit ω -Eq.(8) in Ref.[19]- in our context can be written as

$$\begin{aligned} \tau_\omega \sum_{j=1}^{2dN} \lambda_{\omega(G),j} &= -(dN-1) \int_{\omega(G)} \alpha(S_t \Gamma_{\omega(G)}) \ dt \\ &= -(dN-1) \int_{\omega(G)} \mathbf{c}_{\omega(0)}(S_t \Gamma_{\omega(0)}) \ dt \cdot \mathbf{G} + o(G^2) \ . \end{aligned} \tag{17}$$

Note that for $\mathbf{G} = 0$ the flow does not contract or expand elements of phase space, i.e. $\Lambda_{\omega(G=0)} = 1$ for all UPOs, and each addend in the sums in Eq.(15) vanish. Then, expanding the terms in Eq.(15) in powers of $\mathbf{G}$, and substituting into Eq.(13) we obtain

$$\langle \mathbf{J} \rangle^{(n)}(\mathbf{G}) = \mathbf{A}^{(n)} \mathbf{G} + o(G^2) \ , \tag{18}$$

where $\mathbf{A}^{(n)}$ is the symmetric matrix whose ij-entry is

$$A_{ij}^{(n)} = (dN-1) \frac{\sum_{\omega\in P_n(G)} \Lambda_{\omega(0),u}^{-1} Q_{\omega(0),i} Q_{\omega(0),j}}{\sum_{\omega\in P_n(G)} \tau_{\omega(0)} \Lambda_{\omega(0),u}^{-1}} \ , \tag{19}$$

[7]Observe that time reversal symmetry in the equations of motion is not enough for our purposes (see e.g. Ref.[25]). The equations of motion of our models are time reversible for all $\mathbf{G}$, however the corresponding attractors and repellers may cover disjoint regions of phase space if $\mathbf{G}$ is sufficiently large. In that case, taking the time reverse image of a point in the attractor produces a point in the repeller, and it is not true then that $-\omega \in P_n(G)$ if $\omega \in P_n(G)$. On the contrary, the time reverse of a UPO in $P_n(G)$ is still in $P_n(G)$, if the attractor is dense (as in Anosov systems). Systems with non dense attractors can be studied (see e.g. Ref[25]), but they do not concern us here, as we are interested in the small fields regime.

[8]Given $n \in \mathbb{N}$, it may happen that there are no UPOs in $P_n(G)$ with $\int_\omega \alpha(S_t\Gamma_\omega) dt > 0$, in which case $P_n^+(G)$ is empty and the sums in Eqs.(15) vanish. If this happens for all n greater or equal to a given n_0, then $\langle \mathbf{J} \rangle_\Omega = 0$, and our calculations leading to Eq.(23) trivially hold.

and $Q_{\omega(0),i}$ is defined by

$$Q_{\omega(0),i} = \int_{\omega(G)} c_{\omega(0),i}(S_t \Gamma_{\omega(0)}) \; dt \; . \tag{20}$$

Thus, if we differentiate the k-th component of the approximate current, $\langle J_k \rangle^{(n)}(\mathbf{G})$, with respect to G_l say, we obtain

$$\partial_{G_l} \langle J_k \rangle^{(n)}(\mathbf{G}) = A_{kl}^{(n)} + o_1(G) = A_{lk}^{(n)} + o_2(G) = \partial_{G_k} \langle J_l \rangle^{(n)}(\mathbf{G}) + o_3(G) \; , \tag{21}$$

where the $o_i(G)$, $i = 1, 2, 3$, are distinct quantities of order G. Let us denote by

$$L_{kl} \equiv \partial_{G_l} \langle J_k \rangle_\Omega |_{\mathbf{G}=0} = \partial_{G_l} \lim_{n\to\infty} \langle J_k \rangle^{(n)} \Big|_{\mathbf{G}=0} \; , \tag{22}$$

the kl-entry in the transport coefficients tensor, and recall that the sequence $\{\langle J_k \rangle^{(n)}(\mathbf{G})\}_{n=1}^\infty$ converges to a limit (Assumption 1) uniformly (Assumption 2), as $n \to \infty$. Then, we have (Assumptions 1. and 2.)

$$L_{kl} = \partial_{G_l} \lim_{n\to\infty} \langle J_k \rangle^{(n)} \Big|_{\mathbf{G}=0} = \lim_{n\to\infty} \partial_{G_l} \langle J_k \rangle^{(n)} \Big|_{\mathbf{G}=0} = L_{lk} \; ; \quad k, l = 1, ..., \nu \; . \tag{23}$$

These are the Onsager relations for our systems, and we can state that:

Theorem 1 *For thermostatted N particle systems verifying Assumptions 1. and 2. the following holds*

$$L_{kl} = L_{lk} \qquad \textit{for all} \quad k, l = 1, ..., d \; . \tag{24}$$

As mentioned above, we note that the geometry at hand may improve our calculations, thanks to ensuing symmetries of the corresponding systems. By geometry we mean all the specifications which have to do with the shape of the particles and of the medium in which they move. In most cases, these are such that reversing the direction of $\mathbf{G}$ effectively amounts to just a rotation of the coordinate axes. In other words, the UPOs embedded in the attractor corresponding to $-\mathbf{G}$ have the same properties as those in the attractor corresponding to $\mathbf{G}$, except for having an opposite cumulative current: i.e. for every $n \in I\!N$, and for every $\omega(G) \in P_n(G)$ there is $\omega(-G) \in P_n(-G)$ such that

$$\tau_{\omega(-G)} = \tau_{\omega(G)} \; ; \quad \Lambda_{\omega(-G),u}^{-1} = \Lambda_{\omega(G),u}^{-1} \; ; \quad \mathbf{I}_{\omega(-G)} = -\mathbf{I}_{\omega(G)} \; . \tag{25}$$

Observe that this has nothing to do with time reversal invariance, although it may appear to be similar. Equations (25) are a consequence of the geometry of the system only, and express what can be referred to as the $[\mathbf{G} \to -\mathbf{G}]$-field reversal symmetry, which may not obtain for anisotropic systems. Therefore, having distinguished the time reversal invariance from the (possibly not present) field reversal symmetry, we see that the second is not needed for the validity of the Onsager reciprocity relations. If, on the other hand, Eqs.(25) hold, Assumption 2. can be taken in the sense of full analyticity,[9] and the terms $\mathbf{I}_{\omega(G)}(\Lambda_{\omega(G),u}^{-1} - \Lambda_{-\omega(G),u}^{-1})$ of Eq.(15) are odd in $\mathbf{G}$, while the terms $\tau_{\omega(G)}\Lambda_{\omega(G),u}^{-1}$ of Eq.(9) are even in $\mathbf{G}$. Then, Eq.(18) can be re-written as

$$\langle \mathbf{J} \rangle^{(n)}(\mathbf{G}) = \mathbf{A}^{(n)}\mathbf{G} + o(G^3) \tag{26}$$

making our calculations correct to second order, rather than just first order in the field. However, such field reversal symmetry is not needed for the derivation of the OR.

[9] For instance, in Ref.[2] full analyticity of α around $\mathbf{G} = 0$ is assumed.

2.4 Nonnegativity of transport coefficients

Here, we generalize an argument recently proposed in Ref.[19]. Let us consider the transport coefficient associated with the k-th current:

$$\sigma_k = \partial_{G_k} \langle J_k \rangle_\Omega |_{G=0} = L_{kk} \ , \qquad k = 1, ..., \nu \ . \tag{27}$$

Then, in view of Eq.(7), and grouping terms as in Eq.(15), allows us also to deduce the fact that σ_k cannot be negative. To see that, rewrite Eq.(7) as

$$\langle J_k \rangle_\Omega (\mathbf{G}) = \lim_{n\to\infty} \frac{\sum_{\omega \in P_n^+(G)} \Lambda_{\omega,u}^{-1} I_{\omega,k} \left[1 - \Lambda_\omega\right]}{\sum_{\omega \in P_n(G)} \tau_\omega \Lambda_{\omega,u}^{-1}} = \sum_{i=1}^{\nu} A_{ki} G_i + o(G^2) \ ; \quad k = 1, ..., \nu \tag{28}$$

which implies $\sigma_k = A_{kk}$. This quantity, in turn, is nonnegative as it results from taking the limit $A_{kk} \equiv \lim_{n\to\infty} A_{kk}^{(n)}$ in Eq.(19) (the limit exists because of Assumptions 1. and 2.). Therefore, we can state this as

Theorem 2 *For thermostatted N particle systems satisfying Assumptions 1. and 2, $\sigma_k \geq 0$, for all $k = 1, ..., \nu$.*

For this result Assumptions 1. and 2. are enough. On the contrary, the problem of the strict positivity of σ_k does depend on further conditions, similarly to the situation investigated in Ref.[20].

We conclude this section by observing that all our results are not purely dynamical in nature: they rest on the choice of the initial ensemble, which must evolve into the stationary SRB measure by the given dynamics. Indeed, initial conditions such that the consequent evolution violates our conclusions are possible. However, Assumption 1. says that such initial conditions are very special, because they only constitute a set of zero Lebesgue measure. We also observe that the identification made in Eq.(3) seems to require a large number of particles N, in order to make physical sense (see Ref.[26]).

3 Discussion

The purpose of this section is to put forward possible problems/open questions in our approach, in order to stimulate further research.

1. First of all, we have tried to look into the results of Refs.[1, 2, 3] from a different perspective, and we have found that (for the purpose of this work) the assumptions of those papers could be replaced by others. Indeed, rather than saying that our systems are Anosov-like (or axiom A-like), we merely use one representation of the average currents, Eq.(7), which would be correct for all smooth functions if the systems were really Anosov, and we postulate that the currents associated with UPOs are well behaved. This is similar to equilibrium statistical mechanics where rather than specifying the expected chaotic properties of the given systems, the form of the ensembles are postulated, and calculations are developed afterwards with such ensembles. One advantage of that might be that we do not really have to know which properties of the dynamics of particle systems make them "Anosov-like". In particular, smoothness of the dynamics, hyperbolicity etc. may not be strictly necessary, as several examples seem to indicate, especially if only selected functions of phase are considered. For instance, the Lorentz gas has singularities (although it is strongly hyperbolic); while the Ulam map is not hyperbolic.

Yet, POE have performed correctly when applied to such systems (see Ref.[27] for the Ulam map). See also Ref.[28], in which intermittent diffusion is treated in terms of cycle expansions.

2. Another advantage of our approach is precisely the fact that the special representation of the stationary state which we use −that based on orbital measures− can actually and succesfully be implemented in the simplest particle systems (various periodic Lorentz gas models), at least in the calculations of several quantities [7, 15, 16, 17, 18, 21]. For the same reason, our predictions formulated in terms of POE are amenable to direct tests via computer simulations of such systems.

3. In all approaches, ours as wel as those of Refs.[1, 2, 3], the necessity of having a large number of particles seems to be absent. Classical proofs of the Onsager relations always relied upon the assumption that the system is large (made of $N \approx 10^{23}$ particles), and that it can be split into small "local" ones; basic variables $a_1, ..., a_n$, with $n \ll N$ were associated with these small local subsystems ($n \approx 10^{10}$ say). The origin of this apparent paradox is the assumed equality of the average phase space contraction and macroscopic entropy production rates, which only seems to hold for large N, Ref.[26].

4. In the paper we have avoided the problem of dealing with the singular points of the dynamics of systems of hard particles, saying that they would only get vanishing weights in the POE Eq.(7). In the Appendix, we give an argument to support this point of view. If that is correct, and orbits with grazing collisions effectively do not spoil the POE-representation of the stationary distributions, because they do not contribute to Eq.(7), then we have evidenced one possible mechanism through which the techniques devised for axiom-A systems remain valid in more general settings, e.g. those of Refs.[7, 15, 16, 17, 18, 21].

Appendix

Here we argue that in case of hard core interactions, UPOs with grazing collisions can be neglected in the expansion Eq.(7), so that they do not endanger the validity of Assumptions 1. and 2. First of all, the largest Lyapunov exponent of one such orbit would appear to be very large (effectively infinite) in numerical simulations; hence a very small (effectively vanishing) weight would be assigned to such orbits (see e.g. Ref.[29]). Indeed, consider the trajectories of two particles which are going to experience a grazing collision. If a perturbation moves the trajectories of the two particles a little away from the colliding path, there will be no collision at all, while there will be a non grazing collision if the perturbation moves the trajectories closer to each other.

Moreover, for the Lorentz gas at equilibrium, these ideas can be supported by an analytical argument. The Lyapunov exponents, in this case, are obtained from the logarithms of the eigenvalues of products of matrices of the following form:[10]

$$\mathcal{M} \equiv \prod_{j=1}^{n} \mathcal{M}_j \ , \tag{29}$$

if n is the number of collisions, where

$$\mathcal{M}_j = - \begin{pmatrix} 1 & \frac{2}{\cos\psi_j} \\ l_j & 1 + \frac{2l_j}{\cos\psi_j} \end{pmatrix} \ . \tag{30}$$

[10]This follows from a simple calculation. See, e.g., Ref.[30].

Here, l_j is the distance travelled by the moving particle between the collisions j and $j+1$, and ψ_j is the collision angle at the jth collision, where $\psi_j = 0$ means head on collision, while $\psi_j = \pi/2$ corresponds to a grazing collision. Because $\psi_j \in [0, \pi/2]$, and $\cos\psi_j \geq 0$ for all j, every $\mathcal{M}_j$ is defined and consists of negative entries if $\psi_j \in [0, \pi/2)$ (hard collisions), while it is not defined for grazing collisions.

Let us compute $\mathcal{M}$ for an orbit with n collisions, and $\psi_j < \pi/2$ for all $j = 1, ..., n$, and denote by

$$\mathcal{M}^{(n-1)} = \prod_{j=1}^{n-1} \mathcal{M}_j \equiv (-1)^{n-1} \begin{pmatrix} a & b \\ c & d \end{pmatrix} , \tag{31}$$

the product of the first $(n-1)$ blocks. The terms a, b, c and d are then finite, positive numbers. Now, multiply $\mathcal{M}^{(n-1)}$ by $\mathcal{M}_n$, the matrix of the last free flight and collision, in order to obtain $\mathcal{M}$:

$$\mathcal{M} = \mathcal{M}_n \mathcal{M}^{(n-1)} = (-1)^n \begin{pmatrix} 1 & 2/\cos\psi_n \\ l_n & 1 + 2l_n/\cos\psi_n \end{pmatrix} \begin{pmatrix} a & b \\ c & d \end{pmatrix} \tag{32}$$

$$= (-1)^n \begin{pmatrix} a + \frac{2c}{\cos\psi_n} & b + \frac{2d}{\cos\psi_n} \\ al_n + c\left(1 + \frac{2l_n}{\cos\psi_n}\right) & bl_n + d\left(1 + \frac{2l_n}{\cos\psi_n}\right) \end{pmatrix} . \tag{33}$$

The eigenvalues of $\mathcal{M}$ obey

$$\Lambda_u + \Lambda_s = \mathrm{Tr}(\mathcal{M}) = (-1)^n \left(a + d + bl_n + \frac{2}{\cos\psi_n}(c + dl_n)\right) , \tag{34}$$

and

$$\Lambda_u \Lambda_s = \det(\mathcal{M}) = \pm 1 . \tag{35}$$

Hence, the determinant remains bounded, while the magnitude of the trace grows without limits if $\psi_n \to \pi/2$, which implies that one of the eigenvalues becomes very large, while the other becomes very small. The result is that the weight Λ_u^{-1} in Eq.(7) gets smaller and smaller, and converges to zero for UPOs with ψ_n closer and closer to $\pi/2$.

This argument is not yet a full proof that orbits with grazing collisions can be neglected in the POE, since we have not explained in which sense one such orbit could be considered as the limit of a sequence of orbits without grazing collisions. However, the argument shows how a collision which is sufficiently close to grazing contributes to make the weight of the corresponding orbit small and, keeping fixed the other quantities, the weight is the smaller, the closer to grazing the collision is. We conclude noting that the problem posed by trajectories with grazing collisions is present in all approaches based on dynamical weights. In this respect, one of the nice features of the approach based on periodic orbits is that each UPO, as a whole, covers only a *finite* length, hence the relevant stable and unstable manifolds, and the UPO's contribution to the POE can be computed in finitely many steps. This is why the previous analysis for the Lorentz gas can be carried out.

Acknowledgements

This work has been supported in part by GNFM-CNR (Italy), and through the grant "EC contract ERBCHRXCT940460" for the project "Stability and universality in classical mechanics". In particular GNFM-CNR supported one of the author's (EGDC) stay in Torino, where the ideas originated. EGDC also gratefully acknowledges support from the US Department of Energy under grant DE-FG02-88-ER13847.

References

[1] G. Gallavotti, 1996, *Chaotic hypothesis: Onsager reciprocity and fluctuation dissipation theorem*, J. Stat. Phys., **84**, 899

[2] G. Gallavotti, 1996, *Extension of Onsagers reciprocity to large fields and the chaotic hypothesis*, Phys. Rev. Lett., **78**, 4334

[3] G. Gallavotti and D. Ruelle, 1996, *SRB states and nonequilibrium statistical mechanics*, archived in mp_arc @ math.utexas.edu, #96-645

[4] G. Gallavotti and E.G.D Cohen, 1995, *Dynamical ensembles in nonequilibrium statistical mechanics*, Phys. Rev. Lett., **74**, 2694

[5] G. Gallavotti and E.G.D Cohen, 1995, *Dynamical ensembles in stationary states*, J. Stat. Phys., **80**, 931

[6] Ya. G. Sinai, 1972, *Gibbs measures in ergodic theory*, Russian Math. Surveys, **27**, 21. R. Bowen, 1975, *Equilibrium states and the ergodic theory of Anosov diffeomorphisms*, Lecture Notes in Mathematics, Vol.470, Springer Verlag. D. Ruelle, 1976, *A measure associated with axiom A attractors*, Amer. J. Math., **98**, 619.

[7] G. P. Morriss, L. Rondoni and E.G.D. Cohen, 1995, *A dynamical partition function for the Lorentz gas*, J. Stat. Phys., **80**, 35

[8] D.J. Evans, E.G.D. Cohen and G.P. Morriss, 1993, *Probability of second law violations in shearing steady flows*, Phys. Rev. Lett., **71**, 2401

[9] F. Bonetto, G. Gallavotti, P. Garrido, 1996, *Chaotic principle: an experimental test*, archived in mp_arc @ math.utexas.edu, #96-154

[10] S. Lepri, R. Livi and A. Politi, 1997, *Heat transport in anharmonic chains*, preprint

[11] D. Ruelle, 1978, *Thermodynamic Formalism*, Addison-Wesley, Reading, Massachusetts

[12] G. Gallavotti, 1981, *Aspetti della teoria ergodica, qualitativa e statistica del moto*, Pitagora Editrice, Bologna

[13] W. Parry, 1986, *Synchronisation of canonical measures for hyperbolic attractors*, Comm. Math. Phys., **106**, 267

[14] R. Artuso, E. Aurell and P. Cvitanovic, 1990, *Recycling of strange sets: I. Cycle expansions*, Nonlinearity, **3**, 325. *Recycling of strange sets: II. Applications*, Nonlinearity, **3**, 361

[15] P. Cvitanovic, P. Gaspard and T. Shreiber, 1992, *Investigation of the Lorentz gas in terms of periodic orbits*, CHAOS, **2**, 85

[16] W. N. Vance, 1992, *Unstable periodic orbits and transport properties of nonequilibrium steady states*, Phys. Rev. Lett., **69**, 1356

[17] G. P. Morriss and L. Rondoni, 1994, *Periodic orbit expansions for the Lorentz gas*, J. Stat. Phys., **75**, 553

[18] J. Lloyd, M. Niemeyer, L. Rondoni, and G.P. Morriss, 1995, *The nonequilibrium Lorentz gas*, CHAOS, **5**, 536

[19] L. Rondoni and G. P. Morriss, 1997, *Applications of periodic orbit theory to N-particle systems*, J. Stat. Phys., **86**, 991

[20] D. Ruelle, 1996, *Positivity of entropy production in nonequilibrium statistical mechanics*, J. Stat. Phys., **85**, 1

[21] C.P. Dettmann and G.P. Morriss, 1997, *Stability ordering of cycle expansions*, Phys. Rev. Lett., **78**, 4201

[22] W. Hoover, 1986, *Molecular dynamics*, Springer-Verlag, Berlin. D.J. Evans and G.P. Morriss, 1990, *Statistical mechanics of nonequilibrium liquids*, Academic Press, London

[23] N. I. Chernov, G. L. Eyink, J.L. Lebowitz and Ya. Sinai, 1993, *Steady state electric conductivity in the periodic Lorentz gas*, Comm. Math. Phys., **154**, 569

[24] A. Baranyai, D.J. Evans and E.G.D. Cohen, 1993, *Field-dependent conductivity and diffusion in a two-dimensional Lorentz gas*, J. Stat. Phys., **70**, 1085

[25] F. Bonetto and G. Gallavotti, 1996, *Reversibility, coarse graining and the chaoticity principle*, archived in mp_arc @ math.utexas.edu, #96-50

[26] E.G.D. Cohen and L. Rondoni, 1997, (in preparation).

[27] G.P. Morriss and L. Rondoni, 1996, *Chaos and its impact on the foundations of statistical mechanics*, Australian J. Phys., **49**, 51

[28] C.P. Dettmann and P. Cvitanovic, 1997, *Cycle expansions for intermittent diffusion*, (preprint)

[29] M.M. Sano, 1994, , J. Phys. **27A**, 4791

[30] P. Cvitanovic and R. Mainieri, 1997, *Classical and Quantum Chaos: a Cyclist Treatise*, archived in www.nbi.dk/∼ronnie/QCcourse/